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X-RAY DIFFRACTION STUDIES OF DISORDER IN ALLIED SPECTRA-1000 POLYETHYLENE FIBERS

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POLYMER RESEARCH BRANCH

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ABSTRACT

A recent paper by Busing on the X-Ray diffraction study of polyethylene fibers (Busing, Macromolecules, 1990, 23, 4608-4610) has been reviewed and condensed. Busing describes a new and improved method for measuring and analyzing the crystal structure and pertinent morphological parameters of polyethylene in fiber form. More than a determination of structure in a particular fiber, the paper is a pointer to how crystallography may be best accomplished in semicrystalline polymers in the future. The paper outlines the application of FIBLS, the full-pattern least-squares fiber-diffraction program. The results of the analysis include crystallinity, orientation function, paracrystalline disorder parameters, unit cell dimension parameters, atomic positions, bond distances, and bond angles. The most complete analysis using the difference Fourier method reveals, for the first time, three additional sites for carbon atoms in the unit cell structure, partially occupied by disordered segments of the chain bypassing their usual route in the unit cell to alternative sites. The importance of the method goes beyond polyethylene, or even beyond polymers of interest for fibers applications. An X-Ray study of any semicrystalline polymer is improved in terms of experimental precision by studying the material in fiber form. This reduces diffraction line overlap, by separating them into layers, and also improves signal-to-noise ratio by concentrating diffraction intensity. The reviewer suggests that further improvement could be made by using a position-sensitive counter to reduce counting time while improving counting statistics.

X-Ray Diffraction Study of Disorder in Allied Spectra-1000 Polyethylene Fibers

Research by W.R. Busing, Macromolecules, *1990,* 23, *4608*

Condensation and commentary by C. Richard Desper, US Army Materials Technology Laboratory

CONDENSATION OF THE RESEARCH

PURPOSE OF THE STUDY

To define the crystalline structure in highly oriented polyethylene fiber in a more quantitative manner, using the full information available by X-ray fiber diffractometry; additionally, to demonstrate the application of the full-pattern least-squares fiber-diffraction (FIBLS) program

WHAT RESEARCHER ACCOMPLISHED

The paper is much more than a report on polyethylene fiber morphology; it is a pointer to how crystallography should be accomplished in polymers in the future. The author has demonstrated the method for precisely determining, for a polyethylene fiber sample, 1) the crystallinity, 2) the orientation function, 3) the paracrystalline disorder parameters, 4) the unit cell dimension parameters, 5) the atomic positions and their mean square displacements, and 6) the bond distances, bond angles, and the "setting angle" between the unit cell edges and the zigzag carbon–carbon backbone. The method is of general applicability and represents an important advance in polymer diffractometry.

In addition, the author demonstrated the existence of sites in the crystal structure attributable to disorders in the crystal structure, suggesting the wandering of polymer chains laterally in the b direction as well as the usual c direction. This could be due to either internal disorder or could be associated with regular chain folding.

BACKGROUND

Polyethylene is a typical semicrystalline polymer that has been extensively studied over the years. Bunn[1] first determined the basic crystal structure of polyethylene in 1939, then, with Alcock,[2] related the broadening of the diffraction lines to the small crystallite size in the 100–300 Å range. Kavesh and Schultz[3] more closely defined the crystal structure, including paracrystallinity

contributions into the analysis of line broadening for more precise determination of the crystallinity, atomic position parameters, and disorder parameters. However, they worked with bulk unoriented samples, rather than using oriented fiber specimens for possible improvements in the refinement.

Others studying a variety of polymers, for example Allcock et al.,[4] Burkhart et al.,[5] and Grasso et al.,[6] took a different tack, dealing with oriented specimens to separate the diffraction peaks into layers. For the most part, however, such studies worked with data from exposed film rather than from counter diffractometry. thus limiting the precision of their intensity measurements and precluding the possibility of evaluating paracrystalline disorder from line-broadening analysis. In the most sophisticated analysis of such fiber diffraction data, a modeling approach called LALS (*L*inked *A*tom *L*east *S*quares) was used to refine the data and provide the best possible atomic position parameters. Such an approach begins with certain assumptions about the chemical structure and bonding and introduces appropriate starting values for bond lengths. bond angles, and torsional angles before beginning the least squares procedure. Grasso et al.[6] indicate that this method is useful where the data available is not sufficient for a full matrix least squares refinement.

The full matrix least squares refinement of precision polymer fiber diffractometry data has been waiting for someone to put all the pieces together—the diffractometer with its software, and the appropriate least squares refinement software—in order to make the experiment and data analysis possible. With Busing's paper, that wait is over.
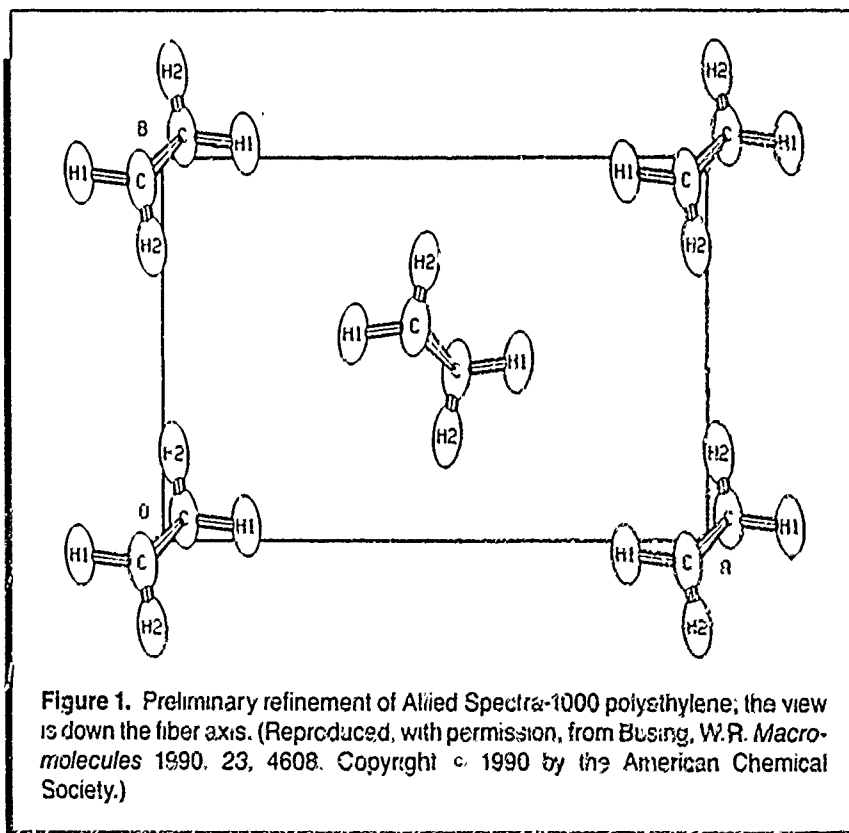
RESEARCHER'S APPROACH

Although computer automated X-ray diffractometry has been available since the 1960s, the needs of polymer crystallography have not been adequately addressed. The methodology developed has been geared towards the single crystal specimen and that methodology has been highly successful, to the point of automating all aspects of data acquisition and many aspects of data analysis. Busing was a vital contributor to these developments—his papers[7,8] pointed out the mathematical and crystallographic algorithms that make possible high-precision single crystal X-ray crystallography on an automated basis.
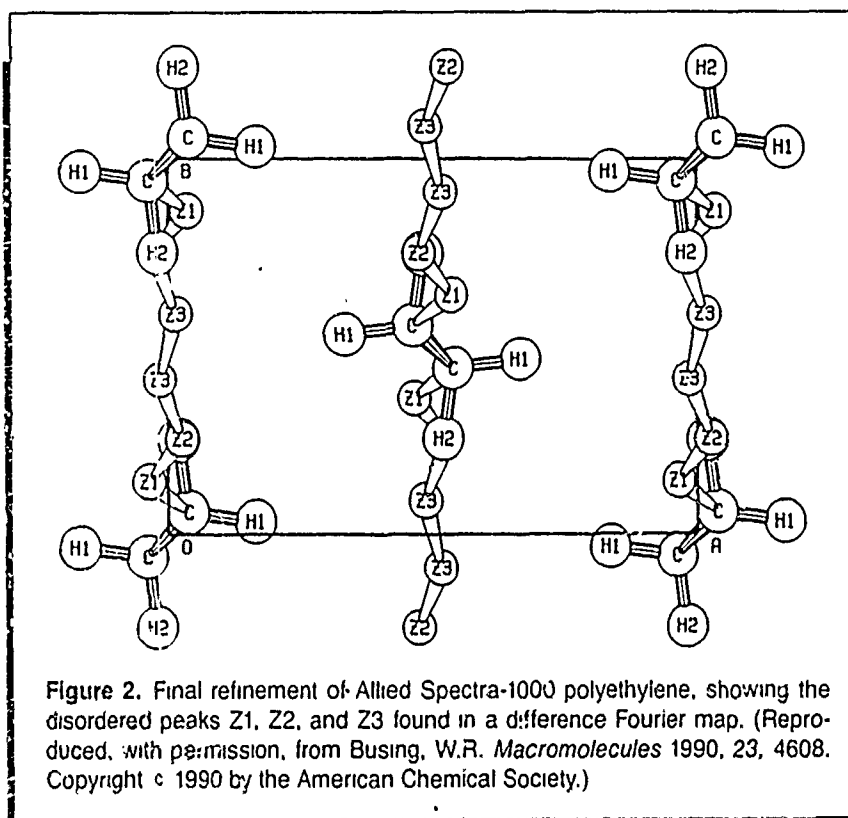
Turning to polymer crystallography, the major shortcoming hindering the structural solution is that, since a multitude of crystals are present, the simple three-dimensional relationships between the positions of various (hkl) reflections is lacking. In the worse case, the polymer is randomly oriented and the data obtainable is strictly one-dimensional (intensity vs. Bragg angle 2θ) and the additional information in orientation space is lost. The use of a polymer specimen in fiber orientation form has always been useful from the point of view of separating the diffraction peaks into layers, thus: 1) separating peaks in different layers that would otherwise overlap in their 2θ range, with loss of precision; 2) improving the signal-to-noise ratio by concentrating crystalline intensity that otherwise spreads over the entire sphere of orientation; and 3) providing, through the separation into crystallographically determined layers, clues to the indexing of the pattern. Admittedly the use of a fiber oriented specimen still does not provide the richness of information of the single crystal diffractometry, since diffraction information over only one (χ) of the two (χ, ϕ) Eulerian angles of orientation is obtained, while the second (ϕ) remains an angle of cylindrical symmetry.

Busing obtained 25 diffraction scans, systematically covering layers 0 through 4, for least squares data analysis. (Note that the layer number l, the third of the Miller indices h, k, and l, may assume noninteger values for this purpose.) Amorphous scattering contributed a varying baseline below all of the diffraction peaks, which is handled as a series of line segments. The program FIBLS fits calculated diffraction curves to all of the data by adjusting peak parameters: peak center positions, peak intensities, and peak shapes. (The background parameters are also adjustable in the refinement.) The parameters refined by the procedure are the unit cell dimensions, disorientation, crystallite size and paracrystallinity, atomic coordinates, anisotropic temperature factors, interatomic distances and angles, and the previously mentioned setting angle of the carbon zigzag in the unit cell.

The initial solution is the packing pattern, viewed down the fiber axis, shown in Figure 1. The size of the ellipsoids depicting the atoms represents the amplitude of thermal vibrations. Busing's numerical refinement results (not shown) are in general agreement with those of previous workers.[3,9,10] Small quantitative differences with earlier work are real but are not further discussed.

One unique result from Busing's analysis is shown in Figure 2, which results from a more complete treatment than that of Figure 1. This difference Fourier map shows additional sites labeled Z1, Z2, and Z3. Such sites are *not* occupied in all such unit cell positions, but have an occupancy factor of 0.1. These partially occupied sites represent disordered atoms—places in the polymer chain where the atoms, rather than following their regular zigzag up the c axis, slip instead to the side to the neighboring crystal unit cell in the b axis direction.

Figure 1. Preliminary refinement of Allied Spectra-1000 polyethylene; the view is down the fiber axis. (Reproduced, with permission, from Busing, W.R. *Macromolecules* 1990, 23, 4608. Copyright © 1990 by the American Chemical Society.)

Figure 2. Final refinement of Allied Spectra-1000 polyethylene, showing the disordered peaks Z1, Z2, and Z3 found in a difference Fourier map. (Reproduced, with permission, from Busing, W.R. *Macromolecules* 1990, 23, 4608. Copyright c 1990 by the American Chemical Society.)

COMMENTARY ON THE RESEARCH

Busing's paper represents a new standard for solving crystallographic problems in semicrystalline polymers. His FIBLS program, the description of which is to be published separately, will no doubt be sought for by others in the field and promises to become a standard tool.

In terms of its quantitative results, the paper corroborates previously used concepts for polyethylene crystallinity: an amorphous fraction, small crystallite size, paracrystalline disorder approaching 2%, and a setting angle of 45.9° between the b axis and the carbon zigzag plane.

In terms of the polyethylene structure, Busing's observation of disorder sites, where (at a 10% probability) a chain departs laterally from the crystal repeat pattern, is the first reported observation of this kind. As such, it points up the value of the new method of X-ray analysis.

The reviewer has one suggestion to offer for improving the method: the use of a position-sensitive proportional counter (PSPC), instead of a simple counter measuring a single intensity at a time, to measure the data. Such a counter records a number of data points (e.g., 500 to 1,000) simultaneously, offering the possibility of obtaining more data of higher precision and resolution in a reasonable experimental time. There is one complication introduced by the use of the PSPC it will not sample the diffraction pattern at fixed values of the layer line number l, except for the zeroth (equatorial) layer. One would need to take this into account in the data acquisition and in the least squares refinement. One can place the center of the PSPC on, for instance, the (011) reflection, where the l value is precisely 1.00. However, because of the geometry of the instrument, the ends of the active detector region will most likely be above

and below that l value. Thus a given layer would need to be covered by a series of PSPC patterns since, for instance, a detector position crossing the (011) diffraction peak would miss the center of the (111) peak by an unacceptable amount. Also, the least squares program must recognize that such a scan is not at a fixed layer value. These factors would have to be taken into consideration in using a PSPC for this purpose, but in the long run, might be worth the effort.

Finally, the reviewer also wishes to call attention to a recent paper presented by Crist and Howard[11] (in press) on the analysis of diffraction patterns in oriented polyethylene. While the method of refinement is not equivalent to Busing's method, both papers deal with line shape analysis to determine crystallite size and paracrystalline disorder parameters A comparison of the results should be of interest.

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